Group theory and octupolar order in URu_2Si_2

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Abstract

Recent experiments on URu_2Si_2 show that the low-pressure hidden order is non-magnetic but it breaks time reversal invariance. Restricting our attention to local order parameters of $5f^2$ shells, we find that the best candidate for hidden order is staggered order of either $\mathcal{T}_z^\beta$ or $\mathcal{T}_{xyz}$ octupoles. Group theoretical arguments for the effect of symmetry-lowering perturbations (magnetic field, mechanical stress) predict behavior in good overall agreement with observations. We illustrate our general arguments on the example of a five-state crystal field model which differs in several details from models discussed in the literature. The general appearance of the mean field phase diagram agrees with the experimental results. In particular, we find that a) at zero magnetic field, there is a first-order phase boundary between octupolar order and large-moment antiferromagnetism with increasing hydrostatic pressure; b) arbitrarily weak uniaxial pressure induces staggered magnetic moments in the octupolar phase; and c) a new phase with different symmetry appears at large magnetic fields.

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I. INTRODUCTION

The nature of the so-called "hidden order" of the $T < T_0 \approx 17$K phase of URu_2Si_2 has long been debated [1]. Taking strictly on-site local order parameters only, $U^{4+} \rightarrow 5f^2$ shells can carry magnetic dipole, electric quadrupole, magnetic octupole, and even higher multipole order parameters. The full local symmetry is described by $\mathcal{G} = \mathcal{D}_{4h} \otimes \mathcal{G}_t$ where $\mathcal{D}_{4h}$ is the tetragonal point group, and $\mathcal{G}_t = \{\hat{E}, \hat{T}\}$ the two-element group generated by the time reversal operator[2] $\hat{T}$. The classification of the twelve most obvious [3] local order parameters is given in Table I. Being expressed as Stevens equivalents, all order parameters are even under space inversion. The notation "g" and "u" in Table I refers to their parity under time reversal.

TABLE I: Symmetry classification of the local order parameters [4] for $\mathbf{B} = 0$ ($\mathcal{D}_{4h}$ notations [2], overline means symmetrization [5]).

sym (g)	operator	sym (u)	operator
A_{1g}	$\mathcal{E}$	A_{1u}	$\overline{J_x J_y J_z (J_x^2 - J_y^2)}$
A_{2g}	$\overline{J_x J_y (J_x^2 - J_y^2)}$	A_{2u}	J_z
B_{1g}	$\mathcal{O}_2^2$	B_{1u}	$\mathcal{T}_{xyz} = \overline{J_x J_y J_z}$
B_{2g}	$\mathcal{O}_{xy} = \overline{J_x J_y}$	B_{2u}	$\mathcal{T}_z^\beta = \overline{J_z (J_x^2 - J_y^2)}$
E_g	$\{\mathcal{O}_{xz}, \mathcal{O}_{yz}\}$	E_u	$\{J_x, J_y\}$

About 30 years of work on one of the most intensively studied f-electron systems has not brought clarification: the order is still "hidden" [1]. As we are going to describe, theoretical progress has long been held up by the ambiguity of experimental findings on apparently heterogeneous samples. However, crucial recent experiments [6, 7] allow to infer what the equilibrium properties of ideal samples of URu_2Si_2 would be.

From the earliest neutron scattering experiments [8], the issue has been complicated by the observation of apparent f-electron micromagnetism. Ascribing the magnetic moments to the bulk of the sample, the observations indicated two-sublattice $\mathbf{Q} = (0, 0, 1)$ antiferromagnetism of U $5f$-shell moments of $O(0.01\mu_B)$ directed along the tetragonal fourfold axis z in the low-T ($T < T_0$) phase. Though the nominal value of the ordered moment m was two orders of magnitude lower than the paramagnetic moment, this seemed to conform to

the general idea that micromagnetism is the canonical behavior of f-electron systems on the borderline between the non-magnetic (heavy fermion) Kondo state and RKKY magnetism [9]. According to this view, URu_2Si_2 might have been put in the same class as UPt_3 or $CeAl_3$ [10].

Many previous ideas about URu_2Si_2 were based on the assumption that antiferromagnetism with micro-moments is a static phenomenon, and it is an intrinsic feature of the $T < T_0$ phase. Since the ordering of small moments could not account for the large thermal anomalies at the 17K transition, it was assumed that the staggered dipole moment m is a secondary order parameter, being induced by the primary ordering of an un-identified full-amplitude order parameter ψ (the hidden order). This would require that antiferromagnetism has the same symmetry as the hidden order, i.e., ψ should break time reversal invariance and share the spatial character of m under the symmetry classification according to the tetragonal point group [11] $\mathcal{D}_{4h}$. With these assumptions, the Landau free energy functional would contain a term $-m\psi$, generating $m \neq 0$ whenever the primary $\psi \neq 0$. This is a scenario which we are going to discard, for the reasons given below, and further in Sec. II.

The intimate connection between hidden order and micromagnetism looked always somewhat suspicious because the variability $(0.017 - 0.04)\mu_B$ of the antiferromagnetic moment was too large to be associated with nominally good-quality samples, and because the onset of micromagnetism did not exactly coincide with T_0. Susceptibility and NMR under pressure give an insight: though the sample-averaged sublattice magnetization grows with pressure, it seems to arise from the increase in the number of magnetic sites, not from changing the magnetic moment at a given site [12]. This points to the possibility that the apparent micromagnetism is an attribute of heterogeneous samples, and should be understood as ordinary antiferromagnetism of a small ($\sim 1\%$) volume fraction in samples which for some reason always include a minority phase [13].

The argument was clinched by high-pressure μSR experiments: hidden order is non-magnetic, and antiferromagnetism of at least $O(0.1\mu_B)$ ionic moments appears at a first-order transition at $p_{tr} \approx 0.6$GPa (Ref. 6). There are two thermodynamic phases, a non-magnetic phase with $\langle\psi\rangle \neq 0$ and $\langle m\rangle = 0$, and the antiferromagnetic phase with $\langle m\rangle \neq 0$ and $\langle\psi\rangle = 0$. At ambient pressure, the magnetic ($\langle m\rangle \neq 0$) phase is slightly less stable than the phase with hidden order [14]. However, large-amplitude antiferromagnetism is stabilized at hydrostatic

pressures $p > 0.6$GPa following a first order non-magnetic-to-magnetic transition. In a range of low hydrostatic pressures, the nature of the low-temperature phase remains the same as in ambient conditions: $\psi \neq 0$ and $m = 0$. The situation is, of course, different if we apply fields which lower the symmetry of the system: magnetic field $\mathbf{B}$, or uniaxial stress σ.

In the following Sections, we discuss the effect of uniaxial stress, and of magnetic field, on the ordered phases of URu_2Si_2. We will deduce that the low-pressure zero-field order must be staggered octupolar order of either B_{1u} or B_{2u} octupoles (Sec. II). The overall appearance of the temperature - magnetic field phase diagram will be explained (Sec. III). Finally, the general arguments will be illustrated by the results obtained from a new crystal field model (Sec. IV).

II. OCTUPOLAR ORDER

In this Section, we argue that the experimental evidence presented in Refs. 6, 7 unambiguously shows that the "hidden order" of URu_2Si_2 is alternating octupolar order with $\mathbf{Q} = (0, 0, 1)$. Here we restrict our attention to the strictly local (on-site) order parameters [15] listed in Table I. Two-site quadrupole–spin and three-site spin–spin correlators could appear in the same symmetry class as on-site octupoles [16]; the present argument does not differentiate these cases.

Let us recall the hydrostatic pressure – temperature phase diagram obtained from high-pressure μSR experiments [6] (a phase diagram of the same shape results from our mean field theory, see Fig. 5, left). Hidden order $\langle\psi\rangle \neq 0$ is the attribute of the low-pressure, low-temperature phase ($p < p_{\rm tr}$, $T < T_0(p)$). Though all samples show some micromagnetism, it can be safely concluded that this is an extrinsic effect and in a perfect sample, hidden order should be non-magnetic. Antiferromagnetism of at least $O(0.1\mu_{\rm B})$ ionic moments appears at a first-order transition at $p_{\rm tr} \approx 0.6$GPa . At $p < p_{\rm tr}$ the hidden order onset temperature $T_0(p)$, and at $p > p_{\rm tr}$ the Néel temperature $T_{\rm N}(p)$ are critical temperatures for the hidden-order-to-paramagnetic, and the antiferromagnetic-to-paramagnetic transitions, respectively; these meet the first order phase boundary at a bicritical point. It follows that m and ψ are of different symmetry, and the Landau free energy cannot contain a term $m\psi$. The symmetry of ψ must be in any case different from $A_{2u}(\mathbf{Q} = (0, 0, 1))$.

Regarding the absence of magnetism as an established fact, we can also exclude E_u

(magnetic moments perpendicular to the tetragonal z-axis). The remaining choices for the order parameter ψ are: quadrupolar (B_{1g}, B_{2g}, or E_g), octupolar (B_{1u} or B_{2u}), hexadecapole (A_{2g}), or triakontadipole (A_{1u}) (see Table I). Quadrupole and hexadecapole moments are time reversal invariant, while octupoles and triakontadipoles change sign under time reversal.

An important recent experiment allows to decide the time reversal character of the hidden order. Yokoyama et al [7] carried out magnetic neutron scattering measurement in the presence of uniaxial stress applied to a single crystal sample either along, or perpendicular to the tetragonal axis. Stress $\sigma \parallel (001)$ does not produce significant change in magnetic moments. However, for stress $\sigma \perp (001)$ the staggered moment increases approximately linearly, reaching $\sim 0.25\mu_{\rm B}$ at $\sigma = 0.4$GPa. In contrast to hydrostatic pressure, no threshold value is needed to induce a magnetic moment; it appears as soon as the stress σ is finite.

Mechanical stress is time reversal invariant, thus it can produce magnetic moments only from an underlying state which itself breaks time reversal invariance. This limits the choice of hidden order to B_{1u} or B_{2u} (octupolar), or A_{1u} (triakontadipoles). We emphasize that the choice of octupolar order is essentially different from the previously assumed quadrupolar order [17, 18, 19] which does not break time reversal invariance. Additional evidence in favor of the time reversal invariance breaking character of ψ comes from NMR measurements[20].

We will show that the properties of URu_2Si_2 can be described well with the assumption of octupolar order. This would make URu_2Si_2 the third well-argued case of primary octupolar order in an f-electron system (the first two cases being NpO_2 [21] and $Ce_{1-x}La_xB_6$ [22]). Within the limits of our argument, either B_{1u} or B_{2u} would reproduce the basic effect of stress-induced large-amplitude antiferromagnetism. On the other hand, we rule out A_{1u} triakontadipoles as order parameters.

First, we consider stress applied in the (100) direction. $\sigma \parallel (100)$ lowers the symmetry to orthorombic $\mathcal{D}_{2h}$ (see Appendix). Under $\mathcal{D}_{2h}$, $A_{2u}^{\rm tetr} \to B_{1u}^{\rm orth}$ and $B_{2u}^{\rm tetr} \to B_{1u}^{\rm orth}$, so the order parameters $\mathcal{T}_z^\beta$ and J_z become mixed (Table IV). A state with spontaneous $\mathcal{T}_z^\beta$ octupolar order carries J_z magnetic dipole moments as well [23], accounting for the observations [7].

An alternative way to derive this is by inspecting the relevant terms of the Landau potential for the undistorted tetragonal phase (the operators in the equations below have the meaning given in Table I). Choosing B_{2u} octupolar order parameter, consider the mixed

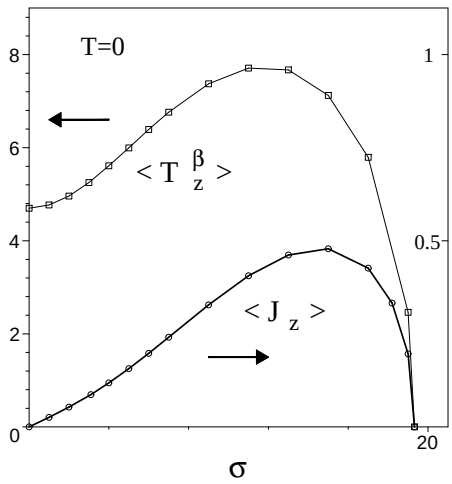

FIG. 1: Stress-induced magnetic moment in the octupolar phase, based on the crystal field model described in Sec. IV. Thick line: $\langle M_z \rangle$ staggered magnetization, thin line: $\langle \mathcal{T}_z^\beta \rangle$ octupolar moment, as a function of the uniaxial pressure $\sigma \parallel (100)$ (σ in arbitrary units).

third order invariant

$$\mathcal{I}(A_{2u}\otimes B_{1g}\otimes B_{2u}) \;=\; c_1 J_z(\mathbf{0})\mathcal{T}_z^\beta(\mathbf{Q})\mathcal{O}_2^2(-\mathbf{Q}) \\ +c_2 J_z(\mathbf{Q})\mathcal{T}_z^\beta(-\mathbf{Q})\mathcal{O}_2^2(\mathbf{0})\,. \qquad (1)$$

Generally, $c_1 \neq 0$ and $c_2 \neq 0$. For our present purpose, the second term matters. A uniform stress $\sigma \parallel (100)$ induces uniform ($\mathbf{q} = \mathbf{0}$) $\mathcal{O}_2^2$ quadrupole density [24] which couples the staggered ($\mathbf{q} = \mathbf{Q}$) B_{2u} octupole order parameter to the J^z dipole density with $\mathbf{q} = -\mathbf{Q}$, i.e., the same spatial modulation. Neutron scattering shows that stress-induced antiferromagnetism has the same simple two-sublattice structure with $\mathbf{Q} = (0, 0, 1)$ that was previously ascribed to micromagnetism, thus the periodicity of the hidden octupolar order must be the same.

The actual stress-dependence of antiferromagnetic polarization depends on microscopic details. Fig. 1 illustrates the general behavior for a crystal field model which we describe in detail later.

Stress applied along the z-axis induces $\mathcal{O}_2^0$ which transforms according to the identity representation A_{1g}, thus it does not appear in the invariants, and it is not predicted to induce magnetism. This is in qualitative accordance with the observation that for $\sigma \parallel (001)$ the induced moments are an order of magnitude smaller than for $\sigma \parallel (100)$. We believe that

the fact that these moments are not exactly zero, is due to non-ideality of the sample, as micromagnetism itself is.

The situation is less clear with varying the direction of stress in the $\sigma \perp (001)$ plane. Experiments find that the stress-induced antiferromagnetic moment is essentially the same for $\sigma\|(110)$ as for $\sigma\|(100)$ [7]. Taken in itself, stress-induced antiferromagnetism would be as easy to understand for $\sigma\|(110)$ as it was for $\sigma\|(100)$. Namely, the invariant expansion of the Landau potential contains also

$$\begin{aligned}\mathcal{I}(A_{2u}\otimes B_{2g}\otimes B_{1u}) \;=\; & c_3 J_z(\mathbf{0})\mathcal{T}_{xyz}(\mathbf{Q})\mathcal{O}_{xy}(-\mathbf{Q}) \\ & + c_4 J_z(\mathbf{Q})\mathcal{T}_{xyz}(-\mathbf{Q})\mathcal{O}_{xy}(\mathbf{0})\,. \end{aligned} \tag{2}$$

$\sigma\|(110)$ induces uniform $\mathcal{O}_{xy}$ quadrupolar polarization. Assuming that the hidden (octupolar) order is $\mathcal{T}_{xyz}(-\mathbf{Q})$, it is coupled to $J_z(\mathbf{Q})$, the same kind of antiferromagnetism as we found before. An alternative way to arrive at the same result is by observing that $\sigma\|(110)$ lowers the symmetry to orthorombic, under which $\mathcal{T}_{xyz}$ and J_z belong to the same irrep (Appendix, Table IV).

We have to emphasize, though, that assuming a homogeneous system, either we have an explanation for the effect at $\sigma\|(100)$ (with $\mathcal{T}_z^\beta$ octupolar order), or for $\sigma\|(110)$ (with $\mathcal{T}_{xyz}$ octupolar order), but not for both. Under tetragonal symmetry, $\mathcal{T}_z^\beta$ and $\mathcal{T}_{xyz}$ belong to different irreps, and therefore these orders cannot coexist. At the level of our present argument, the problem cannot be resolved. We believe that it is not merely a difficulty with our model but it points to a genuine feature of URu_2Si_2. We speculate that the $\mathcal{T}_z^\beta$ and $\mathcal{T}_{xyz}$ orders are sufficiently near in energy, and so samples tend to contain domains of both.

We note that the A_{1u} triakontadipole $\overline{J_x J_y J_z (J_x^2 - J_y^2)}$ (see Table I) would not give rise to stress-induced magnetism and is therefore not a suitable choice as order parameter.

It is worth pointing it out that our present scenario offers an explanation why micromagnetism is always present. This may seem paradoxical since if it were connected with a minority phase only, it would be reasonable to expect that some preparation techniques give single-phase samples, i.e., completely non-magnetic ones. However, we ascribe antiferromagnetism also to the polarization of the primary octupolar phase in a stress field. It can be assumed that the environment of impurities and crystal defects always contains regions with the local stress oriented perpendicularly to the tetragonal main axis, thus there is always some local antiferromagnetism.

III. MAGNETIC FIELD

There have been extensive studies of the effect of an external magnetic field on the phase diagram of URu_2Si_2 [25, 26]. The system is relatively insensitive to fields applied in the x–y plane, while fields $\mathbf{B} \parallel \hat{z}$ have substantial effect: hidden order can be suppressed completely with $B_{\rm cr,1} = 34.7$T. The phase boundary in the B–T plane is a critical line, thus hidden order (or its suitable modification) breaks a symmetry also at $\mathbf{B} \neq \mathbf{0}$. At somewhat higher fields, an ordered phase appears in the field range $B_{\rm cr,2} = 35.8\text{T} < B < B_{\rm cr,3} = 38.8\text{T}$. One possibility is that it is the re-entrance of the $B < B_{\rm cr,1}$ hidden order; however, we are going to argue that the high-field order has different symmetry than the low-field order.

The difference between the previously suggested quadrupolar order [17], and our present suggestion of octupolar order, is sharp at $B = 0$ (Ref. 27). However, a $B \neq 0$ magnetic field mixes order parameters which are of different parity under time reversal (Table II). The reason is that switching on a field $\mathbf{B} \parallel \hat{z}$ lowers the point group symmetry from $\mathcal{D}_{4h} \otimes \mathcal{G}_t$ to an 8-element group isomorphic (but not identical) to $\mathcal{C}_{4v}$ (Ref. 2).

Switching on a field $\mathbf{B} \parallel \hat{z}$, geometrical symmetry is lowered from $\mathcal{D}_{4h}$ to $\mathcal{C}_{4h}$. However, the relevant symmetry is not purely geometrical. Though taken in itself, reflection in the xz plane $\hat{\sigma}_{v,x}$ is not a symmetry operation (it changes the sign of the field), combining it with time reversal $\hat{T}$ gives the symmetry operation $\hat{T}\hat{\sigma}_{v,x}$. The same holds for all vertical mirror planes, and $\mathcal{C}_2 \perp \hat{z}$ axes, thus the full symmetry group consists of eight unitary and eight non-unitary symmetry operations [2]

$$\mathcal{G}(B_z) = \mathcal{C}_{4h} + \hat{T}\hat{\sigma}_{v,x}\mathcal{C}_{4h}\,. \tag{3}$$

We may resort to a simpler description observing that

$$\tilde{\mathcal{G}} = \mathcal{C}_4 + \hat{T}\hat{\sigma}_{v,x}\mathcal{C}_4 \tag{4}$$

is an important subgroup of $\mathcal{G}(B_z)$, and we can base a symmetry classification on it. The multiplication table of $\tilde{\mathcal{G}}$ is the same as that of $\mathcal{C}_{4v}$, and therefore the irreps can be given similar labels. It is in this indirect sense that the symmetry in the presence of a field $\mathbf{B} \parallel \hat{z}$ can be regarded as $\mathcal{C}_{4v}$ (a convention used in Ref. 5). The symmetry classification of the local order parameters valid in $\mathbf{B} \parallel \hat{z}$ is given in Table II. The results make it explicit that the magnetic field mixes dipoles with quadrupoles, quadrupoles with certain octupoles, etc.

TABLE II: Symmetry classification of the lowest rank local order parameters for $\mathbf{B} \parallel \hat{z}$ (notations as for $\mathcal{C}_{4v}$ [2])

Symmetry	basis operators
A_1	1, J_z
A_2	$\overline{J_x J_y (J_x^2 - J_y^2)}$, $\overline{J_x J_y J_z (J_x^2 - J_y^2)}$
B_1	$\mathcal{O}_2^2$, $\mathcal{T}_z^\beta$
B_2	$\mathcal{O}_{xy}$, $\mathcal{T}_{xyz}$
E	$\{J_x, J_y\}$, $\{\mathcal{O}_{xz}, \mathcal{O}_{yz}\}$

In a field $\mathbf{B} \parallel \hat{z}$, there can exist ordered phases with four different local symmetries: A_2, B_1, B_2, and E. The zero-field B_{2u}-type $\mathcal{T}_z^\beta$ octupolar order evolves into the B_1-type $\mathcal{T}_z^\beta$–$\mathcal{O}_2^2$ mixed octupolar–quadrupolar order. If the octupolar order is staggered, it mixes with similarly staggered quadrupolar order: this follows from the first line of Eqn. (1) [28]. The character of the low-field phase is indicated in the ground state phase diagram in Figure 2 (all numerical results are derived from a crystal field model described in Sec. IV, but the validity of our general arguments is not restricted to that particular model). The gradual suppression of octupolar order under field applied in a high-symmetry direction is a well-known phenomenon; a similar result was derived for f^3 ions in Ref. 29. In our calculation, the octupolar phase is suppressed at $B_{\mathrm{cr},1} \approx 34.7$T (Figure 2).

Although we are not familiar with experimental results for the combined effect of hydrostatic pressure and magnetic field, it should follow from our scheme that a critical surface is bounding the phase with staggered B_1 octupolar–quadrupolar order until at sufficiently high pressures, the critical surface terminates by a bicritical line. The high-pressure low-field phase has alternating J_z order like in the zero-field case. Hydrostatic pressure does not change the symmetry of the system, but it can change the numerical values of the coefficients in the expansion of the Landau free energy in terms of invariants. Therefore, generally speaking, we expect continuity with the results found for $p = 1$atm up to a threshold value of the pressure where a first order transition to a phase with different symmetry may take place.

Let us return to the case of $B \parallel \hat{z}$ field effects at ambient pressure. The story of the gradual suppression of the B_1 octupolar–quadrupolar phase is closed by itself; it might have

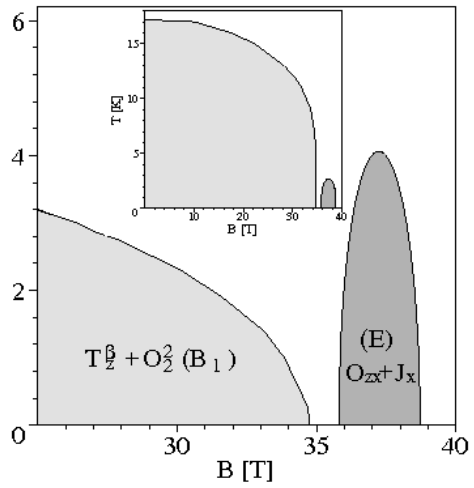

FIG. 2: The high-field part of the $T = 0$ phase diagram of the multipolar model (B in units of T (Tesla)). Vertical axis: $\langle \mathcal{T}_z^{\beta} \rangle$ for the low–field phase, and $\langle \mathcal{O}_{zx} \rangle$ for the high-field phase. The field-induced mixing of the order parameters is shown within the shaded areas. The overall appearance of the T-B (inset, T in units of K) phase diagram is very similar. (The critical temperature of the E phase is scaled up 3-fold).

happened that there is only one ordered phase, surrounded on all sides by the disordered (A_1) phase. However, as shown in Table II, there are order parameters of different (A_2, B_2, E) symmetries; it depends on microscopic details whether such orders are induced by sufficiently high fields. If they are, they cannot coexist with B_1, so the corresponding domains in the B_z–T plane must be either disjoint from the B_1, or, if they are pressed against each other, separated by a first order phase boundary. Our Figure 2 illustrates the former case, where an E phase with mixed quadrupolar–dipolar order (see Table II) is separated from the low-field B_1 phase by a narrow stretch of the disordered phase. We observe that this model result bears a close resemblance to the phase diagram determined by high-field experiments [25, 26]. We note that high-field transport experiments add more phase boundaries to those determined by static experiments [1]. However, it is often found that transport anomalies delineate regions which, while showing interesting differences in the dominant conduction mechanism, still belong to the same thermodynamic phase. Therefore, we take the view that the boundaries shown in Figure 2 are the most robust features of the phase diagram, and the first step should be identifying the nature of these.

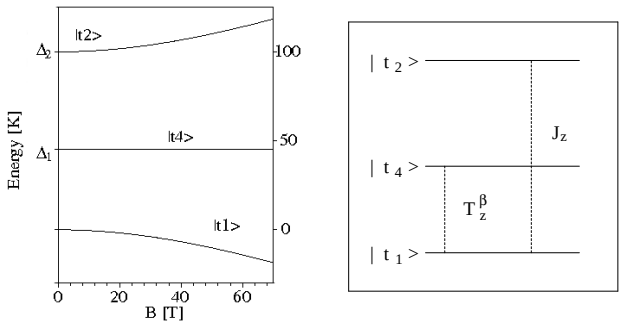

FIG. 3: In the low-field regime, the minimum model consists of three singlets. *Left*: The field-dependence of the levels. *Right*: relevant multipole matrix elements.

An interesting possibility to recover a phase diagram of the same shape would be to identify the high-field phase as the "re-entrance" of the low-field B_1 phase. This possibility was suggested in Ref. 1. However, our present model study does not predict re-entrance.

IV. CRYSTAL FIELD MODEL

The previous arguments were based on a symmetry classification of the order parameters, and the conclusions are independent of the details of the microscopic models that allow the emergence of the ordered phases (in particular, zero-field octupolar order) which we postulate. However, many physical properties (foremost the temperature dependence of the susceptibility, but also the specific heat) were fitted with apparent success by making different assumptions about the nature of the zero-field hidden order (either quadrupolar order of $5f^2$ shells [17, 18, 30], or non-conventional density waves [31]). Therefore it is important to show that our work is not in conflict with findings for which alternative explanations had been suggested but offers fits to the results of standard measurements, which are at least comparable, and in some cases better, than previous results.

Here we assume that equilibrium phases other than the superconducting phase, can be described in terms of localized f-electrons, with stable $5f^2$ shells. We note that for many other interesting f-electron systems (e.g., CeB_6 and Pr-filled skutterudites) the localized-electron description of multipolar ordering works well, in spite of the fact that for certain physical quantities, consideration of the itinerant aspects of f-electron behavior is indispensable.

It is generally agreed [32] that the crystal field ground state is a singlet, and that the salient feature of the level scheme is three low-lying singlets. Three singlets are sufficient to

TABLE III: Tetragonal crystal field states used in the model.

state	form	symmetry	energy[K]
$\|t_2\rangle$	$1/\sqrt{2}(\|4\rangle - \|-4\rangle)$	A_2	100
$\|d_\pm\rangle$	$a\,\|\pm 3\rangle - \sqrt{1-a^2}\,\|\mp 1\rangle$	E	51
$\|t_4\rangle$	$1/\sqrt{2}(\|2\rangle - \|-2\rangle)$	B_2	45
$\|t_1\rangle$	$b(\|4\rangle + \|-4\rangle) + \sqrt{1-2b^2}\,\|0\rangle$	A_1	0

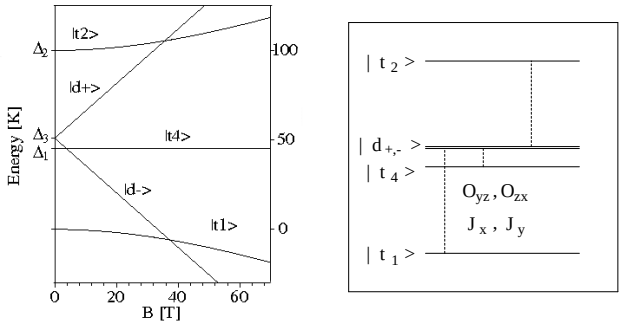

FIG. 4: *Left*: The magnetic field dependence of the single-ion levels in the extended five-state model used up to high values of T and $\mathbf{B}$. *Right*: Additional multipole matrix elements due to the addition of the doublet state to the crystal field levels, which are relevant for the high-field phase.

account for low-energy phenomena. It is found that further two states have to be taken into account to get a satisfactory fit for the susceptibility up to room temperature. We note that the nature of the high-field ordered phase has not been discussed in previous crystal field theories.

The backbone of our crystal field model is the inclusion of the same three singlets as in the works of Santini and coworkers [17, 18, 30], but in different order (Table III, Fig. 3 (left)). The ground state is the $|t_1\rangle$ singlet, and $|t_2\rangle$ an excited state lying at $\Delta_2 = 100$K. $|t_1\rangle$ and $|t_2\rangle$ are connected by a matrix element of J^z, as observed by neutron inelastic scattering [8]. The lower-lying singlet $|t_4\rangle$ is connected to the ground state by an octupolar matrix element: this feature allows the existence of induced octupolar order as the strongest instability of the system (Fig. 3, right). We remark that while other level schemes may also allow octupolar order if one assumes a stronger octupole–octupole interaction, our assumption seems most economical.

Finally, as in previous schemes, at least two further states are needed to fit magnetization

data up to 300K. We found it useful to insert one of the doublets ($|d_\pm\rangle$). This is an alternative to models with five singlets [17, 30]. As we are going to see, fits to standard macroscopic measurements are no worse in our scheme than in previous ones. However, our scheme has the advantage that it accounts for the high-field observations. We show the field-dependence ($\mathbf{B} \parallel \hat{z}$) of the crystal field levels in Fig. 4. The salient feature is the crossing of the (mildly field-dependent) singlet ground state with one of the levels derived from the splitting of the doublet at a field strength lying between the critical fields $B_{\rm cr,2}$ and $B_{\rm cr,3}$. The crossing levels are connected by matrix elements of E operators (Table II). Consequently, we find a high-field E phase where $\{J_x, J_y\}$-type transverse dipolar order is mixed with $\{\mathcal{O}_{zx}, \mathcal{O}_{yz}\}$-type quadrupolar order (see Figure 2).

Commenting on differences between our crystal field scheme (Table III where we use $a = 0.98$, $b = 0.22$) and previously suggested ones, we note that unambiguous determination is very difficult even if an intense experimental effort is undertaken, as in the recent case of Pr-filled skutterudites. By and large we agree with Nagano and Igarashi [33], who argue that the crystal field potential of URu_2Si_2 is not known in sufficient detail yet. We complied with constraints which appear well-founded, as e.g. the neutron scattering evidence by Broholm et al [8], but otherwise we adjusted the model to get low-field octupolar order for which we found model-independent arguments. Level positions were adjusted to get good overall agreement with observations but we did not attempt to fine-tune the model, neither did we check for alternative schemes with less straightforward parametrization.

We use the mean field decoupled hamiltonian

$$\begin{aligned}\mathcal{H}_{\rm MF} = \Delta_1|t_4\rangle\langle t_4| + \Delta_2|t_2\rangle\langle t_2| + \Delta_3 \sum_{\alpha=+,-} |d_\alpha\rangle\langle d_\alpha| \\ -g\mu_{\rm B}BJ_z + \lambda_{\rm oct}\left\langle \mathcal{T}_z^\beta \right\rangle \mathcal{T}_z^\beta - \lambda_{\rm quad}\left\langle \mathcal{O}_{zx}\right\rangle \mathcal{O}_{zx}\end{aligned} \tag{5}$$

where $g = 4/5$, and the octupolar mean field coupling constant $\lambda_{\rm oct}$ is meant to include the effective coordination number; similarly for the quadrupolar coupling constant $\lambda_{\rm quad}$. We assume alternating octupolar order, and uniform $\mathcal{O}_{zx}$ order; the result would be the same if the high-field quadrupolar order is also alternating. We do not introduce independent $\mathcal{O}_2^2$ or $\{J_x,\, J_y\}$ couplings, nevertheless $\langle\mathcal{O}_2^2\rangle \neq 0$ in the B_1 phase, and $\langle J_x\rangle \neq 0$ in the E phase.

At $B = 0$, the only non-vanishing octupolar matrix element is $C = \langle t_1|\mathcal{T}_z^\beta|t_4\rangle \approx 8.8$. Octupolar order is driven by the large C: assuming $\lambda_{\rm oct} = 0.336$K we get the critical temperature $T_0(B = 0) = 17.2$K for $\mathcal{T}_z^\beta$-type antiferro-octupolar order. Using a similar

estimate, we find $\lambda_{\rm oc}^{\rm Np} \approx 0.2$K for NpO_2 which orders at 25K (Ref. 21). The order-of-magnitude correspondence between two documented cases of octupolar order shows that our present estimate of the octupolar coupling strength is not unreasonable.

(5) was solved for all temperatures and fields B_z. We find that the octupolar phase is bounded by a critical line of familiar shape (Fig. 2, inset), which has its maximum $T_0 = 17.2$K at $B_z = 0$, and drops to zero at $B_{\rm cr,1} = 34.7$T. The transition remains second order throughout; we did not hit upon a tricritical point, though we are aware of no reason of why it should not have appeared.

Similarly, the ground-state amplitude of the octupolar order is a monotonically decreasing function of B_z (Fig. 2).

The restricted model with three singlets (Fig. 3) offers two basic choices. In the absence of symmetry-lowering fields, the Landau expansion of the free energy in terms of the order parameters is

$$\begin{aligned} \mathcal{F} \;=\; & \alpha_O(T,p)\langle T_z^\beta\rangle^2 + \beta_O(T,p)\langle T_z^\beta\rangle^4 + \alpha_M(T,p)\langle J_z\rangle^2 \\ & + \beta_M(T,p)\langle J_z\rangle^4 + ... \end{aligned} \tag{6}$$

Note that because of the tetragonal symmetry, the free energy expansion does not contain the term $\langle T_z^\beta\rangle\langle J_z\rangle$. It follows that the possible ordered phases can be (A) $\langle T_z^\beta\rangle \neq 0$ and $\langle J_z\rangle = 0$ or (B) $\langle T_z^\beta\rangle = 0$ and $\langle J_z\rangle \neq 0$. This is in agreement with the experimental finding [6] that (A) is the low-pressure phase, and (B) is the high-pressure phase, and they are separated by a first-order boundary.

This canonical case (qualitatively agreeing with the schematic phase diagram shown in Ref. 6) is illustrated in Fig. 5 (left). It was derived from Eqn. (5) using an ad hoc model assumption about the pressure dependence of the crystal field splittings Δ_1 and Δ_2 (Fig. 5, right) [34]. The shape of the phase boundaries, and in particular the slope of the first order line, could be fine-tuned by adjusting the pressure dependence of the crystal field parameters, but the overall appearance of the phase diagram: two critical lines meeting at a bicritical point, which is also the end-point of a first-order boundary, is generic.

The stress dependence of the induced antiferromagnetic moment (Fig. 1) was determined in a similar calculation, adding the term $-\sigma\mathcal{O}_2^2$ to the Landau potential, and solving the self-consistency equations for $\langle J_z\rangle$ and $\langle \mathcal{T}_z^\beta\rangle$. σ in this calculation has the character of uniaxial stress, but an additional set of experimental data would be needed to determine its absolute

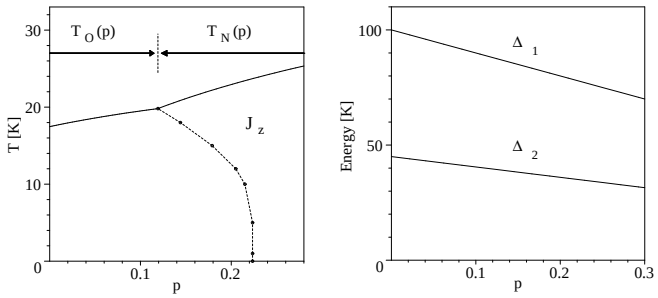

FIG. 5: *Left*: The pressure dependence of the critical temperature of the octupolar and the dipolar antiferromagnetic phases ($T_0(p)$ and $T_N(p)$, respectively). The first-order boundary between the two ordered phases is an interpolation through the calculated points. *Right*: model assumption about the pressure dependence of the crystal field splittings Δ_1 and Δ_2.

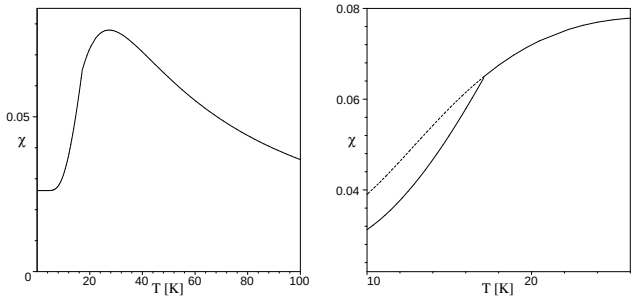

FIG. 6: Linear susceptibility per site (in μ_B/T) on extended temperature scale (left), and in the vicinity of the octupolar transition (right). The dashed line gives the single-ion result.

scale.

Next, we consider the results of some standard low-field measurements. This was not the primary purpose of our work but rather serves as a check. The quadrupolar model [17] obtained a reasonably good fit for the temperature dependence of the linear and non-linear susceptibility in a range of temperature, and we have to prove that our model yields a comparably good description on a completely different microscopic basis.

The octupolar transition shows up as a discontinuity of the linear susceptibility (Fig. 6). This character of the χ_1 anomaly is expected from general arguments [35]. While the low-temperature behavior, including the regime around T_0, is satisfactorily described by the three-state model (Fig. 3), fitting the susceptibility up to room temperature (Fig. 6, left) requires the five-state model (Fig. 4). One of the hallmarks of the hidden-order transition

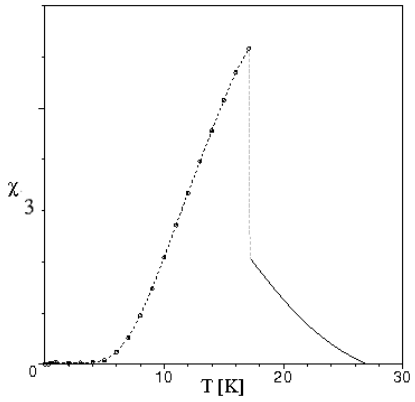

FIG. 7: The temperature dependence of the nonlinear susceptibility χ_3 in the vicinity of the octupolar transition. The dashed line is an interpolation through the calculated points

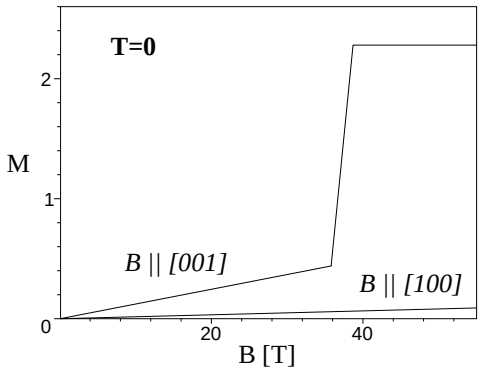

FIG. 8: The magnetization curve at $T = 0$ (M in units of $\mu_{\rm B}$).

of URu_2Si_2 is the strong jump of the non-linear susceptibility χ_3 (Ref. 36). The shape of the calculated anomaly (Fig. 7) corresponds rather well to the experimental result.

Next we discuss the high-field behavior at $B > B_{\rm cr,1}$, and interpret the disjoint high-field phase observed in experiments [25, 26] as a mixed quadrupolar–dipolar phase (the E phase in Fig. 2). We exploit the field dependence of the ionic levels in the five-level model (Table III, Fig. 4). The single-ion levels t_1 and d_- would cross at $B_{\rm cross} = 37.3$T. Since $|t_1\rangle$ and $|d_-\rangle$ are connected by E operators including $\mathcal{O}_{zx}$ (see Fig. 4, right), a range of fields centered on $B_{\rm cross}$ is certain to favour $\{\mathcal{O}_{zx}, \mathcal{O}_{yz}\}$ quadrupolar order, and simultaneous $\{J_x, J_y\}$ dipolar order. We chose a weak quadrupolar interaction $\lambda_{\rm quad} = 0.054$K in Eqn. (5); this gives quadrupolar order between the critical fields $B_{\rm cr,2} = 35.8$T and $B_{\rm cr,3} = 38.8$T. The amplitude of quadrupolar order is not small (Fig. 2) but the ordering temperature is low

($\sim$ 1K) because the coupling is weak. The E phase shows up as the steep part of the magnetization curve in Fig. 8. For $\lambda_{\rm quad} = 0$ we would have a jump-like metamagnetic transition at $B = B_{\rm cross}$.

We are aware of an unsatisfactory feature of the calculated magnetization curve. Though it is clear that our theory involves three critical fields: $B_{\rm cr,1}$, $B_{\rm cr,2}$, and $B_{\rm cr,3}$, at the lowest of these the anomaly is so weak that it does not show up on the scale of Fig. 8. We get a single-step metamagnetic transition distributed over the width of the high-field quadrupolar phase. The overall height of the step is right, but we do not recover the three-step structure of the transition observed by Sugiyama et al [37].

V. DISCUSSION AND CONCLUSION

There have been many attempts to explain the non-superconducting phases of URu_2Si_2. Though the behavior of f-electrons in this system certainly has itinerant aspects, or perhaps URu_2Si_2 is on the verge of a localized-to-itinerant transition, arguing on the basis of a simple localized electron model can lead to useful results. Namely, crystal field theory conforms to a general symmetry classification of the equilibrium phases, which is expected to apply to a wider range of models, including suitably defined Kondo lattice, or Anderson lattice, models. Our main interest lies in cross-effects like the mixing of order parameters in the presence of external magnetic field, or mechanical stress. Our conclusions rely on symmetry reasoning, and only numerical details depend on the choice of the crystal field model which we use to illustrate the general arguments.

The identification of the low-pressure, low-temperature hidden order of URu_2Si_2 is of basic interest. Starting from the high-temperature tetragonal phase, a symmetry-breaking transition can lead to an ordered phase with the following choices for the local order parameter: A_{2u} and E_u dipoles, B_{1g}, B_{2g}, and E_g quadrupoles, B_{1u}, and B_{2u} octupoles, a A_{2g} hexadecapole, and an A_{1u} triakontadipole [4].

It was always clear that the primary order parameter of URu_2Si_2 cannot be dipolar. The possibility of quadrupolar ordering has been extensively discussed [17]. Higher multipoles have been mentioned in a general context [16, 38], but have not been studied in detail.

A recent μSR study [6] finds that the symmetry of hidden order is different from $A_{2u}(\mathbf{Q})$ which is the symmetry of the high-pressure antiferromagnetic phase (the same structure

was ascribed to the supposed "micromagnetism" of URu_2Si_2, which is now understood to be extrinsic). The present experimental status is that the intrinsic low-pressure behavior of URu_2Si_2 is purely non-magnetic. Furthermore, a number of recent experiments proves that the hidden order breaks time reversal invariance, so it cannot be quadrupolar [7, 20, 38]. In particular, Yokoyama et al [7] found that uniaxial stress (which is time reversal invariant) induces large-amplitude antiferromagnetism, which breaks time reversal invariance. It is clear that stress must have acted on a medium which itself was non-invariant under time reversal: it must have been the octupolar phase [39].

We emphasize that stress-induced antiferromagnetism arises only if the stress is uniaxial, and perpendicular to the (001) direction. For tetragonal symmetry, octupoles (B_{1u} and B_{2u}), and dipoles (A_{2u} and E_u) are of different symmetry and therefore they do not mix. It follows that hydrostatic pressure cannot induce antiferromagnetism unless the pressure is high enough to lead to a completely different (purely dipolar) phase via a first-order phase transition. This was found in Ref. [6]. In contrast, uniaxial pressure perpendicular to the tetragonal main axis lowers the symmetry to orthorombic, allowing the mixing of dipoles and octupoles.

We postulated that the hidden order is $\mathcal{T}_z^\beta$ staggered octupolar order (Sec. II). Uniaxial pressure $\sigma\|(100)$ leads to the appearance of J_z dipolar order of the same periodicity. The model works the same way if we postulate $\mathcal{T}_{xyz}$ staggered octupole order, in which case a stress $\sigma\|(110)$ gives J_z antiferromagnetism. Since the octupoles $\mathcal{T}_z^\beta$ and $\mathcal{T}_{xyz}$ belong to different one-dimensional irreps of the tetragonal symmetry (B_{2u} and B_{1u}, respectively), in our theory a homogeneous system can show only one of the stress-induced effects. We hypothesized that the observed near-equivalence of the stress effect in (100) and (110) directions [7] reflects the presence of both kinds of order in a multi-domain structure.

The same assumption about $\mathcal{T}_z^\beta$ octupolar order explains the behavior in applied magnetic field (Sec. III). A field $\mathbf{B}\|(001)$ mixes $\mathcal{T}_z^\beta$ octupoles with $\mathcal{O}_2^2$ quadrupoles. Symmetry breaking is well-defined in the presence of magnetic field, and the transition to hidden order (now a mixed octupolar–quadrupolar order) remains second order up to a critical field $B_{\mathrm{cr},1}$ where $T_0(B) \to 0$.

We illustrated the symmetry arguments on the example of a crystal-field model (Sec. IV). The model has two versions: low-energy phenomena can be described by using three low-lying singlets, while for high energies (or fields, or temperatures) we need five states (the

previous three singlets plus a doublet). The three singlets are the same as in Santini's work, but their sequence was chosen to give an octupolar matrix element between the ground state and the first excited state. The presence of the doublet level is not essential at low fields (and low temperatures) but it splits in a magnetic field $\mathbf{B}\|(001)$, and for a range of high fields, even weak quadrupolar coupling can give quadrupolar order which competes with the low-field octupolar order. We argued that the high-field order observed between 35T and 38T [25, 26] is of quadrupolar nature, with a symmetry different from that of the low-field order.

To conclude, we presented arguments showing that octupolar order of either B_{2u} or B_{1u} symmetry is the zero-field "hidden order" of URu_2Si_2 at ambient conditions. We limited the discussion to strictly on-site order parameters in a localized electron model with stable $5f^2$ valence. However, within this restriction our scenario is compatible with the present knowledge about the phase diagram in the temperature–pressure–field space. The time reversal invariance breaking nature of the order is manifest in the effect that uniaxial pressure applied in certain directions can induce large-amplitude antiferromagnetism.

Acknowledgments

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APPENDIX: ORTHOROMBIC SYMMETRY

Quadrupolar moments couple to external stress. For instance, applying stress $\sigma\|(100)$, $\mathcal{O}_2^2$ quadrupolar moments are induced, while $\sigma\|(110)$ induces $\mathcal{O}_{xy}$. At the same time, the application of uniaxial stress lowers the symmetry from the tetragonal $\mathcal{D}_{4h}$ to one of its subgroups, changing the symmetry classification of all order parameters. This effect is described below.

When we apply uniaxial pressure in direction (100), the previous C_4, S_4, C_2'' and σ_v

cease to be symmetry operations and the residual symmetry is described by the group $\mathcal{D}_{2h}$. The corresponding classification of the order parameters is given in Table IV. We observe that under the new symmetry, the $\mathcal{T}_z^\beta$ octupolar and the J_z dipolar moments mix with each other, and this means that if the system possesses spontaneous staggered $\mathcal{T}_z^\beta$ octupolar order, applying $\sigma\|(100)$ stress induces staggered J_z dipolar moments.

TABLE IV: Symmetry classification of the local order parameters for $\sigma\|(100)$ (*left part*) and for $\sigma\|(110)$ (*right part*). The subscripts g and u mean the even and odd under time reversal. $H_z^\alpha = \overline{J_x J_y (J_x^2 - J_y^2)}$ is one of the nine hexadecapoles.

D_{2h}	
A_{1g}	$\mathcal{O}_2^2$
B_{1g}	$\mathcal{O}_{xy}$, H_z^α
B_{2g}	$\mathcal{O}_{zx}$
B_{3g}	$\mathcal{O}_{yz}$
A_{1u}	$\mathcal{T}_{xyz}$
B_{1u}	$\mathcal{T}_z^\beta$, J_z
B_{2u}	J_x
B_{3u}	J_x

D_{2h}	
A_{1g}	$\mathcal{O}_{xy}$
B_{1g}	$\mathcal{O}_2^2$, H_z^α
B_{2g}	$\mathcal{O}_{yz} - \mathcal{O}_{zx}$
B_{3g}	$\mathcal{O}_{yz} + \mathcal{O}_{zx}$
A_{1u}	$\mathcal{T}_z^\beta$
B_{1u}	$\mathcal{T}_{xyz}$, J_z
B_{2u}	$J_x + J_y$
B_{3u}	$J_x - J_y$

When the uniaxial pressure is applied in (110) directions, it induces $\mathcal{O}_{xy}$ quadrupoles. Now C_4, S_4, C_2' and σ_d have to be omitted from the symmetry group which is again the $\mathcal{D}_{2h}$ point group, only comprised of different elements than in the $\sigma\|(100)$ case. For the present $\sigma\|(110)$ case, the symmetry classification of the order parameters is shown in Table IV. Now the $\mathcal{T}_{xyz}$ octupolar moment mixes with the J_z dipolar moment (if $\mathcal{T}_{xyz}$ is staggered, so is J_z).

When we apply uniaxial pressure along the tetragonal main axis (001), there is no symmetry reduction, the original D_{4h} symmetry classification of the order parameters (Table I) remains valid. Neither the $\mathcal{T}_{xyz}$ nor the $\mathcal{T}_z^\beta$ octupolar moments can induce J_z magnetic moments, since they all correspond to different irreducible representations of the $\mathcal{D}_{4h}$ point

group. An analogous statement holds for the staggered moments.

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[1] N. Harrison, K.H. Kim, M. Jaime, and J.A. Mydosh, Physica B **346-347**, 92 (2004), and references therein.

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[3] These are the twelve lowest-rank multipoles which are needed to get an operator for each of the entries in Table I; they were enumerated, e.g., in Refs. 18, 30. A sufficiently large local Hilbert space would support also order parameters which do not appear in Table I. Though this holds for our five-state-model described in Sec. IV (it supports 24 non-trivial local order parameters, i.e., 12 more than we listed), we do not discuss them because in our interpretation they would correspond to higher-energy processes.

[4] We call local order parameters strictly on-site multipole moments. Pair and three-site correlators can also be defined in terms of localized $5f^2$ models [16] but we do not consider them.

[5] We follow closely the method developed by R. Shiina, H. Shiba, and P. Thalmeier: J. Phys. Soc. Japan **66**, 1741 (1997). See also Ref. 29.

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[11] Notice that this cannot be realized within Table I. Dipoles are either A_{2u}, or E_u; their partners in the same row of Table I are time-reversal-even (E_g quadrupoles and A_{2g} hexadecapoles, respectively). However, in principle suitable A_{2u}, or E_u partners to J_z, $\{J_x, J_y\}$ may be found

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[39] Triakontadipole order is time-reversal-invariance-breaking, but it does not allow the interpretation of the uniaxial stress effect.